Enhancement of nematic order and global phase diagram of a lattice model for coupled nematic systems

D. B. Liarte, and S. R. Salinas

Instituto de Física, Universidade de São Paulo

Caixa Postal 66318, CEP 05314-970, São Paulo, Brazil

04 April 2012

Abstract

We use an infinite-range Maier-Saupe model, with two sets of local quadrupolar variables and restricted orientations, to investigate the global phase diagram of a coupled system of two nematic subsystems. The free energy and the equations of state are exactly calculated by standard techniques of statistical mechanics. The nematic-isotropic transition temperature of system A increases with both the interaction energy among mesogens of system B, and the two-subsystem coupling J. This enhancement of the nematic phase is manifested in a global phase diagram in terms of the interaction parameters and the temperature T. We make some comments on the connections of these results with experimental findings for a system of diluted ferroelectric nanoparticles embedded in a nematic liquid-crystalline environment.

1   Introduction

A dilute suspension of ferroelectric nanoparticles in a liquid-crystalline host has been shown to display an enhancement of the nematic order, with an increase of the isotropic-nematic transition temperature, which is a behavior of interest from the point of view of technological applications [1, 2, 3]. This effect has been explained by the introduction of a coupling between the usual

1

nematic order parameter of the liquid crystals and a set of extra degrees of freedom associated with a coarse-graining average of the electric dipole field produced by the ferroelectric nanoparticles [4, 5]. This work was the motivation to investigate the global phase diagram of a basic Maier-Saupe (MS) model on a lattice with two coupled sets of quadrupolar degrees of freedom.

Although the nematic-isotropic transition is perhaps the most explored transition in liquid crystalline systems, there are still a number of questions and open problems, which can be formulated in terms of simple statistical lattice models. An interesting question is the onset of a biaxial nematic phase [6], which we have recently investigated in the context of a MS model for a mixture of discs and cylinders [7, 8]. Now we analyze the global phase diagram of a similar type of statistical model, with the inclusion of two sets of quadrupolar degrees of freedom, which leads to a connection with the work by Lopatina and Selinger [4, 5]. The nematic MS model is the liquid-crystalline analog of the Curie-Weiss model of ferromagnetism [9, 10, 11]. In this approach, the standard nearest-neighbor interactions between lattice sites are adequately replaced by scaled interactions of infinite range. The statistical-mechanics problem is exactly solvable, and leads to a very convenient framework to perform calculations at the mean-field level. The MS model can be further simplified if we suppose that the local mesogen orientations are restricted to a discrete set of states, according to an early proposal by Zwanzig [12]. Some model calculations with continuous orientations for uniaxial [13], and biaxial [8] nematic systems give support to the idea that this simplification does not lead to qualitatively different results. In recent publications, we have used extensions of this Maier-Saupe-Zwanzig (MSZ) lattice model to investigate the existence of biaxial nematic phases [14, 7, 15] and the thermodynamic properties of nematic elastomers [16].

In Section II we define the MSZ model with two sets of coupled degrees of freedom, and use standard tools of statistical mechanics to write a thermodynamic free energy. This approach has a number of advantages. In contrast with the standard Landau phenomenological approach, the microscopic interactions are explicitly stated and the calculations are not restricted to the neighborhood of the transitions. Also, the model is simple enough to allow exact bona-fide calculations of the free energy and equations of state. In Section III we study the global phase diagram. Contact with a dilute system of ferroelectric nanoparticles embedded in a nematic host is made in Section IV. We then conclude with a summary of the main results, which do support

2

the experimental enhancement of the nematic order.

2 Coupled MSZ model

The energy of a model with two coupled subsystems A and B can be written as

$$\mathcal{H} = E_A + E_B + E_{AB}, \tag{1}$$

where E_A and E_B are given by standard Maier-Saupe soft quadrupolar forms,

$$E_A = -\frac{\varepsilon_A}{N} \sum_{1 \leq i < j \leq N} \sum_{\mu,\nu=x,y,z} \mathcal{A}_i^{\mu\nu} \mathcal{A}_j^{\mu\nu}, \tag{2}$$

$$E_B = -\frac{\varepsilon_B}{N} \sum_{1 \leq i < j \leq N} \sum_{\mu,\nu=x,y,z} \mathcal{B}_i^{\mu\nu} \mathcal{B}_j^{\mu\nu}, \tag{3}$$

with the quadrupole components

$$\mathcal{A}_i^{\mu\nu} = \frac{1}{2} \left(3\, a_i^\mu a_i^\nu - \delta^{\mu\nu} \right), \quad \mathcal{B}_i^{\mu\nu} = \frac{1}{2} \left(3\, b_i^\mu b_i^\nu - \delta^{\mu\nu} \right), \tag{4}$$

where $\{a_i\}$ and $\{b_i\}$ are the respective sets of unit vectors associated with mesogenic units of types A and B, ε_A and ε_B are energy parameters, $\delta^{\mu\nu}$ is a Kronecker symbol, and the coupling term is given by

$$E_{AB} = -\frac{J}{N} \sum_{1 \leq i,j \leq N} \sum_{\mu,\nu=x,y,z} \mathcal{A}_i^{\mu\nu} \mathcal{B}_j^{\mu\nu}, \tag{5}$$

where J is the coupling parameter. Note that the energy global forms for E_A, E_B, and E_{AB} are consistent with the mean-field level of calculations considered in this paper.

In the MSZ model, calculations of the canonical partition function involve sums over the local orientations of the mesogenic units, which are restricted to the six directions along the three Cartesian axes,

$$a_i,\, b_i \in \{(\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)\}. \tag{6}$$

The partition function can be written as

$$
\begin{aligned}
Z &= \sum_{\{a_i\}} \sum_{\{b_i\}} \exp\left\{ \frac{\beta}{2N} \sum_{\mu,\nu} \left[\varepsilon_A \left(\sum_{i=1}^{N} \mathcal{A}_i^{\mu\nu} \right)^2 + \varepsilon_B \left(\sum_{i=1}^{N} \mathcal{B}_i^{\mu\nu} \right)^2 \right. \right. \\
&\quad \left. \left. + 2J \left(\sum_{i=1}^{N} \mathcal{A}_i^{\mu\nu} \right) \left(\sum_{i=1}^{N} \mathcal{B}_i^{\mu\nu} \right) \right] \right\},
\end{aligned} \tag{7}
$$

3

where $\beta = 1/(kT)$ is the inverse temperature, k is the Boltzmann constant, and we have discarded irrelevant terms in the thermodynamic limit. In order to linearize the quadratic forms, we consider the set of identities

$$\int_{-\infty}^{\infty} \prod_{\mu,\nu} (dQ_{\rm A}^{\mu\nu}) \int_{-i\infty}^{i\infty} \prod_{\mu,\nu} \left(\frac{N}{2\pi i} dz_{\rm A}^{\mu\nu}\right) \exp\left[-\sum_{\mu,\nu} z_{\rm A}^{\mu\nu} \left(N Q_{\rm A}^{\mu\nu} - \sum_{i=1}^{N} \mathcal{A}_i^{\mu\nu}\right)\right] = 1, \quad (8)$$

$$\int_{-\infty}^{\infty} \prod_{\mu,\nu} (dQ_{\rm B}^{\mu\nu}) \int_{-i\infty}^{i\infty} \prod_{\mu,\nu} \left(\frac{N}{2\pi i} dz_{\rm B}^{\mu\nu}\right) \exp\left[-\sum_{\mu,\nu} z_{\rm B}^{\mu\nu} \left(N Q_{\rm B}^{\mu\nu} - \sum_{i=1}^{N} \mathcal{B}_i^{\mu\nu}\right)\right] = 1, \quad (9)$$

where we have used the complex representation of the Dirac δ-function. We then write

$$Z = \int [dz] \left[\sum_{\{a_i\}} \exp\left(\sum_i \sum_{\mu,\nu} z_{\rm A}^{\mu\nu} \mathcal{A}_i^{\mu\nu}\right)\right] \left[\sum_{\{b_i\}} \exp\left(\sum_i \sum_{\mu,\nu} z_{\rm B}^{\mu\nu} \mathcal{B}_i^{\mu\nu}\right)\right] \int [dQ]$$

$$\cdot \exp\left\{\frac{\beta N}{2} \sum_{\mu,\nu} \left[\varepsilon_{\rm A} Q_{\rm A}^{\mu\nu 2} + \varepsilon_{\rm B} Q_{\rm B}^{\mu\nu 2} + 2J Q_{\rm A}^{\mu\nu} Q_{\rm B}^{\mu\nu} - \frac{2}{\beta}\left(z_{\rm A}^{\mu\nu} Q_{\rm A}^{\mu\nu} + z_{\rm B}^{\mu\nu} Q_{\rm B}^{\mu\nu}\right)\right]\right\} \quad (10)$$

where $[dz] = \prod_{\mu,\nu} dz_{\rm A}^{\mu\nu} dz_{\rm B}^{\mu\nu}$, $[dQ] = \prod_{\mu,\nu} dQ_{\rm A}^{\mu\nu} dQ_{\rm B}^{\mu\nu}$, and we have discarded contributions to the free energy of $\mathcal{O}(\ln N)$. Since the interaction energies, given by Eqs. (2-5), are of infinite range, the sum over states has been reduced to a simple problem, with decoupled sites, and the final results are of mean-field nature. The sum over the A variables leads to

$$\sum_{\{a_i\}} \exp\left(\sum_i \sum_{\mu,\nu} z_{\rm A}^{\mu\nu} \mathcal{A}_i^{\mu\nu}\right) = \left[\sum_{\{a\}} \exp\left(\sum_{\mu,\nu} z_{\rm A}^{\mu\nu} \mathcal{A}^{\mu\nu}\right)\right]^N$$

$$= \left\{\exp\left[\ln 2 - \frac{1}{2} \sum_{\nu} z_{\rm A}^{\nu\nu} + \ln\left(\sum_{\nu} e^{3z_{\rm A}^{\nu\nu}/2}\right)\right]\right\}^N, \quad (11)$$

which also holds with the exchange A$\leftrightarrow$B.

For large N, the integrals over the Q variables can be obtained by the Laplace method. To leading order, we have

$$I_Q = \exp\left[-\frac{N}{2\beta\left(\varepsilon_{\rm A}\varepsilon_{\rm B} - J^2\right)} \sum_{\mu,\nu} \left(\varepsilon_{\rm B} z_{\rm A}^{\mu\nu 2} + \varepsilon_{\rm A} z_{\rm B}^{\mu\nu 2} - 2J z_{\rm A}^{\mu\nu} z_{\rm B}^{\mu\nu}\right)\right]. \quad (12)$$

4

The stationary point conditions,

$$z_A^{\mu\nu} = \beta\left(\varepsilon_A Q_A^{\mu\nu} + J Q_B^{\mu\nu}\right),$$
$$z_B^{\mu\nu} = \beta\left(\varepsilon_B Q_B^{\mu\nu} + J Q_A^{\mu\nu}\right), \tag{13}$$

which can also be written as

$$Q_A^{\mu\nu} = \frac{\left(\varepsilon_B z_A^{\mu\nu} - J z_B^{\mu\nu}\right)}{\beta\left(\varepsilon_A \varepsilon_B - J^2\right)}, \quad Q_B^{\mu\nu} = \frac{\left(\varepsilon_A z_B^{\mu\nu} - J z_A^{\mu\nu}\right)}{\beta\left(\varepsilon_A \varepsilon_B - J^2\right)}, \tag{14}$$

may be used to switch to the former Q variables. Eqs. (11) and (12) can be used to write the partition function

$$Z = e^{2N\ln 2}\int [dz]\exp\left\{-N\left[\frac{1}{2\beta\left(\varepsilon_A \varepsilon_B - J^2\right)}\sum_{\mu,\nu}\left(\varepsilon_B z_A^{\mu\nu 2} + \varepsilon_A z_B^{\mu\nu 2} - 2J z_A^{\mu\nu} z_B^{\mu\nu}\right)\right.\right.$$
$$\left.\left. + \frac{1}{2}\sum_\nu\left(z_A^{\nu\nu} + z_B^{\nu\nu}\right) - \ln\left(\sum_\nu e^{3z_A^{\nu\nu}/2}\right) - \ln\left(\sum_\nu e^{3z_B^{\nu\nu}/2}\right)\right]\right\}. \tag{15}$$

Note that, on the grounds of mathematical simplicity, we decided to begin the integrations by the Q rather than the z variables.

The complex integrals over the z variables may be done by the method of steepest descents. For $\mu \neq \nu$, the intergral over $z_{\mu\nu}$ gives a contribution of $\mathcal{O}(\ln N)$, which will then be discarded. The saddle-point conditions for the diagonal variables lead to the self-consistent equations

$$Q_A^{\mu\mu} = \frac{1}{2}\left[3\frac{e^{3\beta\left(\varepsilon_A Q_A^{\mu\mu} + J Q_B^{\mu\mu}\right)/2}}{\sum_\nu e^{3\beta\left(\varepsilon_A Q_A^{\nu\nu} + J Q_B^{\nu\nu}\right)/2}} - 1\right], \tag{16}$$

$$Q_B^{\mu\mu} = \frac{1}{2}\left[3\frac{e^{3\beta\left(\varepsilon_B Q_B^{\mu\mu} + J Q_A^{\mu\mu}\right)/2}}{\sum_\nu e^{3\beta\left(\varepsilon_B Q_B^{\nu\nu} + J Q_A^{\nu\nu}\right)/2}} - 1\right], \tag{17}$$

where we have switched to the Q variables using Eqs. (13) and (14). Note that we recover the simple MSZ model in the limit $J \to 0$, and that the $\mathbb{Q}$ tensors are traceless. The free energy is finally written as

$$f = -2kT\ln 2 + \frac{1}{2}\sum_\nu\left(\varepsilon_A Q_A^{\nu\nu 2} + \varepsilon_B Q_B^{\nu\nu 2} + 2J Q_A^{\nu\nu} Q_B^{\nu\nu}\right) - kT$$

$$\cdot\left\{\ln\left[\sum_\nu\exp\left(\frac{3}{2}\beta\left(\varepsilon_A Q_A^{\nu\nu} + J Q_B^{\nu\nu}\right)\right)\right] + \ln\left[\sum_\nu\exp\left(\frac{3}{2}\beta\left(\varepsilon_B Q_B^{\nu\nu} + J Q_A^{\nu\nu}\right)\right)\right]\right\} \tag{18}$$

5

3 Global phase diagram

The equations of state and the free energy are further simplified if we consider the standard parametric form of the order parameter tensors,

$$
\mathbb{Q}_A \equiv \begin{pmatrix} -\frac{1}{2}S_A & 0 & 0 \\ 0 & -\frac{1}{2}S_A & 0 \\ 0 & 0 & S_A \end{pmatrix},
\tag{19}
$$

$$
\mathbb{Q}_B \equiv \begin{pmatrix} -\frac{1}{2}S_B & 0 & 0 \\ 0 & -\frac{1}{2}S_B & 0 \\ 0 & 0 & S_B \end{pmatrix},
\tag{20}
$$

so that

$$
S_A = \frac{1}{2}\left[\frac{3}{1+2\,e^{-9(S_A+JS_B)/4T}}-1\right],
$$
$$
S_B = \frac{1}{2}\left[\frac{3}{1+2\,e^{-9(\varepsilon_B S_B+JS_A)/4T}}-1\right],
\tag{21}
$$

and

$$
\begin{aligned}
f &= -2T\ln 2 + \frac{3}{4}\left[S_A(S_A-2)+\varepsilon_B S_B(S_B-2)+2J(S_A S_B-(S_A+S_B))\right]\\
&\quad -T\ln\left[1+2\,e^{-9(S_A+JS_B)/4T}\right]\left[1+2\,e^{-9(\varepsilon_B S_B+JS_A)/4T}\right].
\end{aligned}
\tag{22}
$$

Note that we have written the free energy f and the energy parameters ε_B and J, as well as the temperature T, in terms of the energy parameter ε_A.

Assuming $\varepsilon_B < \varepsilon_A$, we can write an expansion of the free energy f in terms of S_A, up to $\mathcal{O}(S_A{}^2)$,

$$
f = -2\,T\ln 6 + \frac{3}{16}\frac{(3\varepsilon_B-3J^2-4T)}{(3\varepsilon_B-4T)^2\,T}\left[9J^2-(3-4T)(3\varepsilon_B-4T)\right]S_A{}^2,
\tag{23}
$$

so that the coefficient of $S_A{}^2$ is proportional to $T-T^*$, where T^* is given by

$$
T^* = \frac{3}{8}\left(1+\varepsilon_B+\sqrt{(1+\varepsilon_B)^2+4(J^2-\varepsilon_B)}\right).
\tag{24}
$$

If we suppose that the coefficients of higher powers of S_A in (23) are weakly dependent on temperature, T^* is associated with the spinodal temperature

6

of a Landau-de Gennes theory of nematics, and establishes the threshold of stability of the isotropic phase. For $\varepsilon_B \to 0$, the spinodal temperature is given by $T^* = 1 + \sqrt{1 + J^2}$, which increases with the coupling parameter J, and is thus an indication of the enhancement of the nematic phase. For $\varepsilon_B \to 1$, T^* increases approximately linearly with J. The global behavior is shown in the diagram of Fig. 1, in terms of ε_B, J, and T^*. In particular, the coefficient of $S_A{}^2$ becomes proportional to $(T - 3/4)$ in the limit of zero coupling between the subsystems, $J \to 0$, in agreement with previous results for the simple Maier-Saupe-Zwanzig model [7].
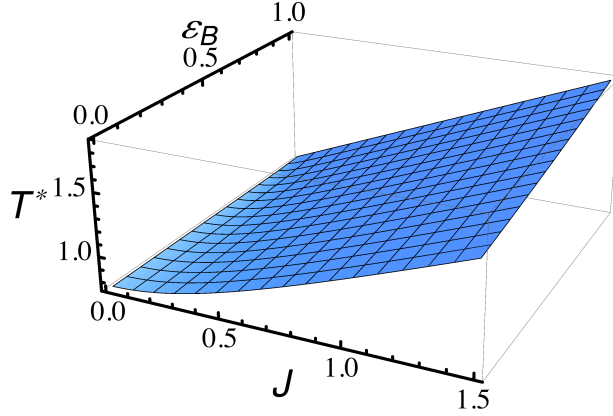

Figure 1: Stability threshold of the isotropic phase in terms of the spinodal temperature T^* and the energy parameters ε_B and J. The isotropic phase is unstable below the surface.

In Fig 2, we show the global phase diagram of this model in terms of the temperature T and the energy parameters ε_B and J, obtained from numerical solutions of the exact equations of state (21) and free energy (22). The transition from the nematic (low-temperature) to the isotropic (high-temperature) phase is of first order, with a jump in both nematic order parameters S_A and S_B. The nematic phase is enhanced by the increase of the energy parameters ε_B and J. As it should be anticipated, this surface is very similar to the threshold of stability of the isotropic phase.
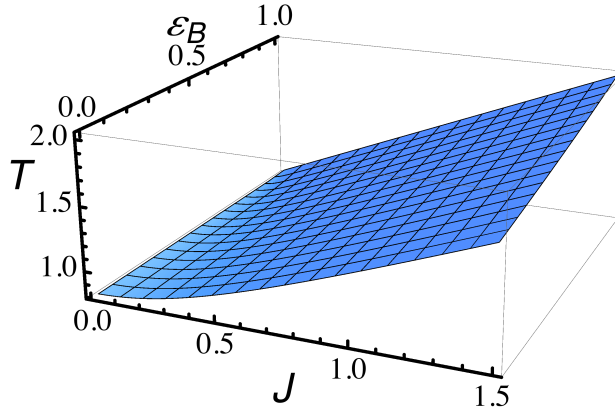
Figure 2: Global phase diagram in terms of temperature T and energy parameters ε_{B} and J. The transition from the nematic (below the surface) to the isotropic phase (above the surface) is discontinuous, with a jump in the nematic order parameters S_{A} and S_{B}.

4   Suspensions of ferroelectric nanoparticles in nematic systems

A coupled system of two types of nematic subsystems has been considered by Lopatina and Selinger to represent a dilute suspension of ferroelectric nanoparticles in a nematic host [4, 5]. The mechanism behind this mapping is the effect on the nematic mesogenic units of the dipole aligning electric fields produced by the ferroelectric nanoparticles. For a range of parameters, assuming uniform nematic order, one may integrate out the position variables, and thus eliminate the complicated spatial dependence of the interactions between mesogens and nanoparticles. It is then possible to associate a nematic-like order parameter with the distribution of orientations of the dipole moments of the nanoparticles. The energy of interaction turns out to be proportional to $S_{\mathrm{LC}} \cdot S_{\mathrm{NP}}$, where S_{LC} and S_{NP} represent the nematic order parameters of the liquid crystal and nanoparticle systems respectively [4, 5], and which has essentially the same form as the coupling energy of Eq. (5). Though the interaction among the nanoparticles has dipole symmetry, one expects the limit $\varepsilon_{\mathrm{B}} \to 0$ will approximately represent a situation in the
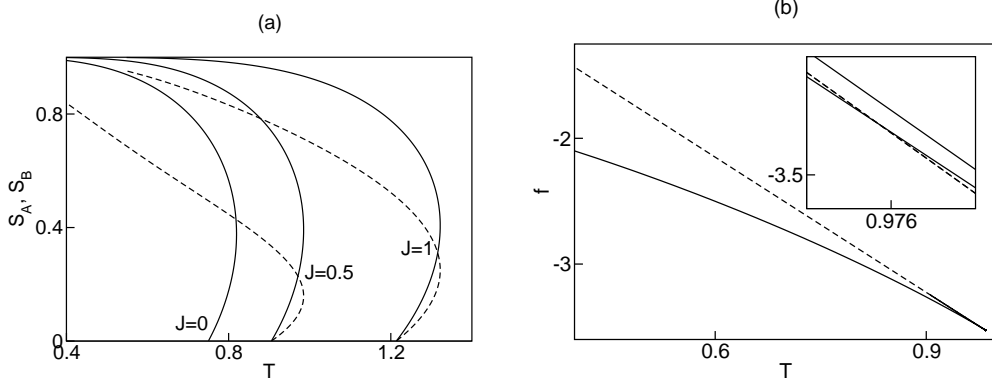
8

dilute regime.

Figure 3: (a) Nematic order solutions for S_A (full curves) and S_B (dashed curve) as a function of temperature for $\varepsilon_B = 0$, and some values of J. There may be up to three solutions: stable nematic, unstable nematic, and isotropic ($S = 0$). The transition from the nematic (upper solution) to the isotropic phase ($S = 0$) takes place where the two free energies become equal. (b) Free energy as a function of temperature for the stable and unstable nematic (full curves) and the isotropic solution (dashed curve), with $\varepsilon_B = 0$ and $J = 0.5$. The inset shows a magnification of the region where the stable nematic and the isotropic solutions have the same free energy.

In Fig 3a we show the nematic solutions for S_A (full curves) and S_B (dashed curves) as a function of temperature, for $\varepsilon_B = 0$ and some values of the coupling parameter J. In general, there may be up to three solutions, two nematic and one isotropic. The lower curve is unstable, and the nematic-isotropic transition takes place at the temperature at which the stable nematic (upper curve) and isotropic ($S = 0$) free energies become equal. The free energies for the three solutions are shown in Fig 3b, for $J = 0.5$. In agreement with some previous experimental [2] and theoretical studies [4, 5, 3], the nematic order is enhanced by the coupling with an ordered subsystem B, which may be interpreted as representing the set of local orientations of ferroelectric nanoparticles. Note that our model always predicts an increase of T_{NI} with the addition of ferroelectric nanoparticles, even though a scenario where the nematic-isotropic transition temperature decreases has also been observed [17]. This scenario is probably suppressed by the assumption of

9

uniform nematic order around the nanoparticles, which our model inherits from Lopatina and Selinger's derivation of the nematic-nanoparticle coupling [4, 5].

5   Summary

We have used a Maier-Saupe-Zwanzig lattice model to study a coupled system of two types of nematic subsystems. The model is simple enough to allow an exact calculation of the free energy. In contrast to the usual phenomenological approaches, it explicitly contains the microscopic energy parameters involved in the nematic-isotropic transition. We show that the nematic-isotropic transition temperature of subsystem A increases with both the interaction energy among mesogens of system B and the two-subsystem coupling J. We draw the global phase diagram in terms of the temperature T and the energy parameters. For non-interacting mesogens in system B, this model may be used to describe the experimentally observed enhancement of the nematic ordering produced by ferroelectric nanoparticles suspended in a liquid-crystalline host.

References

[1] Y. Reznikov, O. Buchnev, O. Tereshchenko, V. Reshetnyak, A. Glushchenko and J. West, App. Phys. Lett. **82**, 1917 (2003).

[2] F. Li, O. Buchnev, C. I. Cheon, A. Glushchenko, V. Reshetnyak, Y. Reznikov, T. J. Sluckin, and J. L. West, Phys. Rev. Lett. **97**, 147801 (2006).

[3] M. V. Gorkunov and M. A. Osipov, Soft Matter **7**, 4348 (2011).

[4] L. M. Lopatina and J. V. Selinger, Phys. Rev. Lett. **102**, 197802 (2009).

[5] L. M. Lopatina and J. V. Selinger, Phys. Rev. E **84**, 041703 (2011).

[6] G. R. Luckhurst, Nature **430**, 413 (2004).

[7] E. do Carmo, D. B. Liarte and S. R. Salinas, Phys. Rev. E **81**, 062701 (2010)

[8] E. F. Henriques and S. R. Salinas, Eur. Phys. J. E **35**, 14 (2012).

[9] M. Kac, in *Statistical physics, phase transitions, and superfluidity*, edited by M. Chrétien, E. P. Gross, and S. Deser (Gordon and Breach, New York, 1968) p. 241.

[10] H. G. Stanley, *Phase Transitions and Critical Phenomena* (Oxford University Press, Oxford, 1971).

[11] S. R. Salinas and W. F. Wreszinski, *Disorder and Competition in Soluble Lattice Models* (World Scientific, Singapore, 1993).

[12] R. Zwanzig, J. Chem. Phys. **39**, 1714 (1963).

[13] M. J. de Oliveira and A. M. F. Neto, Phys. Rev. A **34**, 3481 (1986).

[14] E. F. Henriques and V. B. Henriques, J. Chem. Phys. **107**, 8036 (1997).

[15] E. do Carmo, A. P. Vieira and S. R. Salinas, Phys. Rev. E **83**, 011701 (2011).

[16] D. B. Liarte, S. R. Salinas and C. S. O. Yokoi, Phys. Rev. E **84**, 011124 (2011).

[17] O. Kurochkin, H. Atkuri, O. Buchnev, A. Glushchenko, O. Grabar, R. Karapinar, V. Reshetnyak, J. West and Y. Reznikov, Condensed Matter Physics **13**, 33701:1 (2010).